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Crystal structure of phenarsazine chloride acetic acid solvate, $C_{14}H_{13}AsClNO_2$

Table 1: Data collection and handling.

Crystal:	Green needles
Size:	$0.57 \times 0.11 \times 0.07$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.65 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12,346, 3435, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3118
$N(\text{param})_{\text{refined}}$:	178
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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Abstract

$C_{14}H_{13}AsClNO_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.7180(7)$ Å, $b = 8.2190(7)$ Å, $c = 11.9620(10)$ Å, $\alpha = 87.438(4)^\circ$, $\beta = 73.450(4)^\circ$, $\gamma = 72.167(4)^\circ$, $V = 691.66(10)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0203$, $wR_{\text{ref}}(F^2) = 0.0541$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized upon the recrystallization of phenarsazine chloride from hot glacial acetic

acid. Crystals suitable for the diffraction studies were obtained upon cooling of the solution to room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2 U_{\text{eq}}(C)$.

The H atoms of the methyl group were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [3]), with $U(H)$ set to $1.5 U_{\text{eq}}(C)$.

The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [3]), with $U(H)$ set to $1.5 U_{\text{eq}}(O)$.

The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

Comment

The effect of size and steric hindrance of large ions on chemical and spectroscopic properties of compounds have been a focus of research for many decades. Among the many effects associated with the spatial requirements of counterions have been the glass transition temperature in ionomers [6], surfactant modifying properties [7], the charge transfer

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
As1	0.00496 (2)	0.312269 (18)	0.293392 (12)	0.02873 (6)
Cl1	−0.17051 (5)	0.14354 (5)	0.26643 (3)	0.03300 (9)
N1	0.14376 (19)	0.11283 (16)	0.50831 (11)	0.0293 (3)
H71	0.169 (3)	0.056 (2)	0.5632 (17)	0.040 (5)*
C11	0.2286 (2)	0.13103 (18)	0.29625 (12)	0.0267 (3)
C12	0.2633 (2)	0.05636 (17)	0.39836 (12)	0.0259 (3)
C13	0.4281 (2)	−0.08185 (19)	0.38971 (14)	0.0312 (3)
H13	0.4516	−0.1350	0.4584	0.037*
C14	0.5557 (2)	−0.1408 (2)	0.28286 (15)	0.0363 (3)
H14	0.6669	−0.2342	0.2783	0.044*
C15	0.5238 (2)	−0.0654 (2)	0.18137 (15)	0.0395 (4)
H15	0.6130	−0.1061	0.1077	0.047*
C16	0.3622 (2)	0.0682 (2)	0.18865 (13)	0.0349 (3)
H16	0.3403	0.1195	0.1192	0.042*
C21	−0.0989 (2)	0.35162 (17)	0.45842 (12)	0.0264 (3)
C22	−0.0190 (2)	0.25111 (17)	0.53955 (12)	0.0262 (3)
C23	−0.1072 (2)	0.2915 (2)	0.65904 (13)	0.0324 (3)
H23	−0.0545	0.2241	0.7149	0.039*
C24	−0.2697 (2)	0.4280 (2)	0.69596 (14)	0.0360 (3)
H24	−0.3283	0.4534	0.7772	0.043*
C25	−0.3492 (2)	0.5292 (2)	0.61610 (16)	0.0374 (4)
H25	−0.4608	0.6238	0.6421	0.045*
C26	−0.2637 (2)	0.49007 (19)	0.49924 (15)	0.0333 (3)
H26	−0.3177	0.5588	0.4444	0.040*
O901	0.2404 (2)	0.5009 (2)	−0.02779 (18)	0.0679 (4)
H901	0.1690	0.4427	−0.0303	0.102*
O902	−0.0334 (2)	0.70098 (19)	0.03518 (16)	0.0653 (4)
C90	0.1390 (3)	0.6554 (3)	0.00838 (15)	0.0456 (4)
C91	0.2483 (4)	0.7744 (3)	0.01386 (18)	0.0602 (6)
H91A	0.2979	0.8108	−0.0648	0.090*
H91B	0.3543	0.7159	0.0454	0.090*
H91C	0.1649	0.8748	0.0646	0.090*

in radical ions [8] and polymer-modified electrodes [9], as well as the structural and vibrational spectroscopic behaviour of DNA building blocks [10]. Gaining crystallographic information about a vast variety of large anions has seen significant growth upon the introduction of bulky cations that have simplified the crystallization of these compounds. [11], as for instance showed for chlorido coordination compounds of gallium that incorporate cations derived from the phenarsazine scaffold [12, 13].

At the onset of a research project aimed at the characterization of large anionic compounds, we set out to create a novel set of phenarsazine-inspired cations *via* phenarsazine chloride as the starting material. To confirm the successful synthesis of the latter, a diffraction study of the compound recrystallized from acetic acid was conducted. Very recently, we have determined the molecular and crystal structures of the arsenic-based compound as the DMSO solvate [14]. Furthermore, the molecular and

crystal structures of solvent-free phenarsazine chloride and bromide [15] as well as the *para*-xylene solvate of phenarsazine chloride [16] are available in the literature.

The crystal structure shows the presence of the desired phenarsazine chloride product as well as one molecule of acetic acid in the asymmetric unit. The As–Cl bond length of 2.3022(4) Å is slightly longer than the most commonly reported arsenic–chlorine bond lengths deposited with the Cambridge Structural Database [17]. The angles around the arsenic atom were measured at 97.18(4)° and 97.96(4)° towards the chlorine atom as well as 96.76(6)° for the intracyclic angle thus ruling out classical hybridization of the heavier pnictogen atom. The least-squares planes as defined by the respective atoms of the two aromatic moieties on the one hand as well as the central six-membered heterocyclic ring on the other hand enclose angles of 3.13(7)° and 3.48(7)°, while the two planes of the outer aromatic moieties intersect at an angle of 6.18(7)°.

In the crystal, classical hydrogen bonds of the O–H...O type and the N–H...Cl type are observed next to C–H...O and C–H...Cl contacts. The O–H...O hydrogen bonds give rise to the familiar pattern of dimers among the carboxylic acid groups of the acetic acid solvate molecule, whose descriptor in terms of graph-set analysis [18, 19] requires a $R_2^2(8)$ motif at the unary level. The N–H...Cl hydrogen bonds also give rise to the formation of centrosymmetric dimers with an $R_2^2(12)$ motif. The latter descriptor is also required to describe the C–H...Cl contacts that is supported by one of the hydrogen atoms on the aromatic moieties in *meta*-position to the arsenic atom. The corresponding *meta*-located hydrogen atom on the other aromatic system acts as donor in C–H...O contacts involving the keto-type oxygen atom of the solvent molecule. The methyl group of the acetic acid molecule, in turn, gives rise to C–H...Cl contacts. The graph-set descriptor for the latter two types of contacts is, invariably, D at the unary level. The structure is further characterized by π ... π stacking with the shortest distance between two centers of gravity apparent between the two different aromatic rings measured at only 3.6565(9) Å. In total, the entities of the title compound are connected to undulated double sheets along [1 1 1].

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References

1. Bruker. *APEX2, SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Farrugia L. J. *WinGX and ORTEP for Windows*: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
4. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. *Mercury CSD 2.0* – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* 2008, *41*, 466–470.
5. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
6. Enokida J. S., Hu W., Fang H., Morgan B. F., Beyer F. L., Winter H. H., Coughlin E. B. Modifying the structure and dynamics of ionomers through counterion sterics. *Macromolecules* 2020, *53*, 1767–1776.
7. Oh S. G., Shah D. O. Effect of counterions on the interfacial tension and emulsion droplet size in the oil/water/dodecyl sulfate system. *J. Phys. Chem.* 1993, *97*, 284–286.
8. Piotrowiak P., Miller J. R. Counterion effects in intramolecular charge transfer in radical anions. *J. Phys. Chem.* 1993, *97*, 13052–13060.
9. Mathias M. F., Haas O. Effect of counterion type on charge transport at redox polymer-modified electrodes. *J. Phys. Chem.* 1993, *97*, 9217–9225.
10. Minguiraba A., Vamhindi B. S. D. R., Koyambo-Konzapa S. J. b, Nsangou M. Effects of counterions and solvents on the geometrical and vibrational features of dinucleoside-monophosphate (dNMP): case of 3',5'-dideoxycytidine-monophosphate (dDCMP). *J. Mol. Model.* 2020, *26*, Article no. 99; <https://doi.org/10.1007/s00894-020-04369-6>.
11. Roof L. C., Kolis J. W. New developments in the coordination chemistry of inorganic selenide and telluride ligands. *Chem. Rev.* 1993, *93*, 1037–1080.
12. Burford N., Ragogna P. J., Sharp K., McDonald R., Ferguson M. J. Arsinophosphonium cations from arsenium-phosphine and -bisphosphine coordination chemistry. *Inorg. Chem.* 2005, *44*, 9453–9460.
13. Conrad E., Burford N., Werner-Zwanziger U., McDonald R., Ferguson M. J. Phosphinopnictinophosphonium frameworks. *Chem. Commun.* 2010, *46*, 2465–2467.
14. Averdunk A., Hosten E. C., Betz R. The molecular and crystal structure of phenarsazine chloride dimethylsulfoxide solvate, $C_{14}H_{15}AsClNOS$. *Z. Kristallogr. NCS.* accepted.
15. Fukuyo M., Nakatsu K., Shimada A. The crystal and molecular structure of 10-halo-5, 10-dihydrophenarsazine. *Bull. Chem. Soc. Jpn.* 1966, *39*, 1614–1615.
16. Camerman A., Trotter J. 115. Stereochemistry of arsenic. Part XIII. 10-chloro-5,10-dihydrophenarsazine. *J. Chem. Soc.* 1965, 730–738; <https://doi.org/10.1039/jr9650000730>.
17. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
18. Bernstein J., Davis R. E., Shimon L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.
19. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.